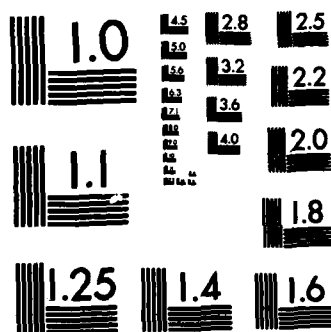END

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. Parameters for Surface-Attached Reactants

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Joseph T. Hupp and Michael J. Weaver
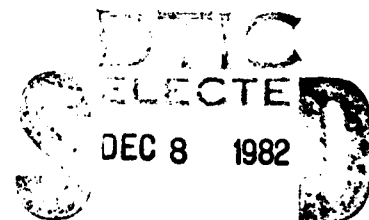
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The interpretation of activation parameters for electrochemical reactions involving surface-attached or adsorbed reactants is considered, and compared with the corresponding experimental quantities for solution-phase reactants. The relation between the experimental activation parameters and the theoretically relevant quantities describing the energetics of heterogeneous electron transfer is summarized; this relationship is shown to be especially straightforward for surface-attached reactants.

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In the past few years there has been considerable interest in electrochemical systems involving reactants attached directly to electrode surfaces.[1-3] Most research efforts have been directed towards the syntheses and structure of attached-molecule systems. However, some work is starting to appear on the redox reactivity of these molecules.[4-11] These studies should yield new insights concerning the dynamics of electron transfer at electrodes by providing critical tests of contemporary theories.[12-14] Comparisons of relative charge transfer rates for reactions of redox species in the attached state and in solution have proved useful in understanding the influence of surface attachment on electron-transfer energetics.[7,8,11]

Further information about particular factors such as Franck-Condon barriers and nonadiabatic effects may be gained by measuring activation parameters. Although the interpretation of activation parameters for electrochemical processes involving solution reactants has been discussed at length[15,16] there is some confusion in understanding their significance for reactions of surface-attached molecules.[7,8] It therefore seems timely to consider the interpretation of activation parameters for this special case.

There are two alternative formulations of electrochemical activation parameters that are especially useful.[15-17] The so-called "ideal" parameters ΔH_i^* and ΔS_i^* are those derived from the temperature dependence of the rate constant measured at a constant metal-solution (Galvani) potential difference ϕ_m.[15,16] Although strictly speaking it is not possible to control ϕ_m as the temperature is varied, in practice this can be achieved to a good approximation by using a nonisothermal cell arrangement where the reference electrode is held at a fixed temperature, allowing ΔH_i^* and ΔS_i^* to be reliably determined.[16] These quantities are of fundamental interest since they equal the enthalpic and entropic barriers to electron transfer at the particular

electrode potential at which they are evaluated. However, it is more common to determine so-called "real" activation parameters ΔH_r^* and ΔS_r^* which are obtained from the temperature dependence of the standard rate constant k°, i.e., the rate constant measured at the standard potential *at each temperature*[‡]. Despite earlier assertions to the contrary, ΔH_r^* and ΔS_r^* have been shown to have particular significance for simple electrode reactions since they represent the enthalpic and entropic barriers at the standard potential that remain after correction for the enthalpic and entropic driving forces, ΔH_{rc}° and ΔS_{rc}°, respectively, for the electrode reaction.[15] Thus the corresponding "ideal" and "real" activation parameters measured for a given electrode reaction at the standard potential are related by[15]

$$\Delta H_i^* = \Delta H_r^* + \alpha T \Delta S_{rc}^\circ \tag{1}$$

and

$$\Delta S_i^* = \Delta S_r^* + \alpha \Delta S_{rc}^\circ \tag{2}$$

where α is the measured transfer coefficient (≈ 0.5) for the overall electrode reaction.

Relationship between Activation Parameters for Surface-Attached and Bulk Solution Reactants

According to the formalism originally due to Marcus[18] the measured rate constant k_{sol}^E (cm sec^{-1}) for a one-electron reduction reaction involving a bulk solution reactant at an electrode potential E can be written as[17,19,20]

$$RT \ln k_{sol}^E = RT \ln A_{sol} - \Delta G_{int}^* - [\Delta G_p^\circ + \alpha_I(\Delta G_s^\circ - \Delta G_p^\circ)] - [\alpha_I F(E - E_{sol}^f)] \tag{3}$$

[‡]Most generally, "real" activation parameters are defined as those obtained at a fixed *overpotential* at each temperature.[15]

In Eq. (3) E_{sol}^f is the formal potential of the solution redox couple concerned,

ΔG_p° and ΔG_s° represent the free energies required to form the precursor and

successor states from the bulk reactant and product, respectively, α_I is the

"intrinsic" transfer coefficient (i.e. the symmetry factor for the elementary

electron-transfer step), A_{sol} is a frequency factor (cm sec^{-1}), and ΔG_{int}^* is the

so-called "intrinsic barrier". This last term equals the activation free

energy for the elementary step in the absence of a free energy driving force,

i.e. when the work terms ΔG_p° and ΔG_s°, and the overall driving force $F(E-E_{sol}^f)$,

each equal zero. The factor A_{sol} represents the frequency with which the

reactant is able to surmount this activation barrier starting from the bulk

solution state.

The determination of the frequency factor and intrinsic barrier contributions

to k_{sol} is therefore of central fundamental interest. In principle, this

may be achieved by measuring the temperature dependence of k_{sol} measured at

E_{sol}^f, k_{sol}°, whereupon the last term in Eq. (3) will vanish. The "real"

activation enthalpy, $\Delta H_{r,sol}^*$, derived in this manner can therefore be expressed

as

$$\Delta H_{r,sol}^* = -R[\frac{d \ln k_{sol}^\circ}{d(1/T)}] = \Delta H_{int}^* + [\Delta H_p^\circ + \alpha_I(\Delta H_s^\circ - \Delta H_p^\circ)] \tag{4}$$

where ΔH_p° and ΔH_s° are enthalpic components of the work terms ΔG_p° and ΔG_s°,

and ΔH_{int}^* is the "intrinsic" activation enthalpy for the elementary

electron-transfer step. This last quantity is the activation enthalpy that

remains when the enthalpic driving force ΔH_{et}° for this step equals zero.

The last term in brackets in Eq. (4) accounts for the contribution to $\Delta H_{r,sol}^*$

arising from the steps involving precursor state formation and successor

state decomposition that precede and follow the rate-determining electron-

transfer step.

It is conventional to determine an accompanying "preexponential" factor A'_{sol} by using the expression

$$k^\circ_{sol} = A'_{sol} \exp(-\Delta H^*_{r,sol}/RT) \qquad (5)$$

However, in view of Eqs. (3) and (4), the desired "true" frequency factor A_{sol} differs from A'_{sol} since the latter contains an activation entropy contribution:

$$A'_{sol} = A_{sol} \exp(\Delta S^*_{r,sol}/R) \qquad (6)$$

Similarly to the "real" activation enthalpy, $\Delta S^*_{r,sol}$ equals the activation entropy that remains after correction for the overall entropic driving force ΔS°_{rc}. This "real" activation entropy is closely related to the "intrinsic" activation entropy ΔS^*_{int} that appears in electron transfer theory.[15,16] However, strictly speaking $\Delta S^*_{r,sol}$ will differ from ΔS^*_{int} since the latter equals the activation entropy for the *elementary step* after correction for the entropic driving force, ΔS°_{et}, for this step. Given that ΔS°_{et} is related to ΔS°_{rc} by $\Delta S^\circ_{et} = \Delta S^\circ_{rc} + \Delta S^\circ_p - \Delta S^\circ_s$, where ΔS°_p and ΔS°_s are the entropic components of the work terms ΔG°_p and ΔG°_s, $\Delta S^*_{r,sol}$ is related to ΔS^*_{int} by [cf. Eq. (4)]

$$\Delta S^*_{r,sol} = \Delta S^*_{int} + [\Delta S^\circ_p + \alpha_I(\Delta S^\circ_s - \Delta S^\circ_p)] \qquad (7)$$

Equations (4)-(7) therefore illustrate a serious interpretative difficulty with activation parameters for solution reactants in that the theoretically significant parameters ΔH^*_{int}, ΔS^*_{int}, and A_{sol} can only be extracted from the experimental kinetics if the enthalpic and entropic components of the work terms ΔG°_p and ΔG°_s can be estimated. In favorable cases the coulombic part of these terms may be obtained for outer-sphere reactions from a knowledge of the diffuse-layer potentials as a function of temperature.[16] However, aside from possible deficiencies in the conventional Gouy-Chapman-Stern treatment used to estimate such work terms, major contributions to the entropic

and enthalpic components may arise from differences in the reactant-solvent interactions within the interfacial reaction site from those in the bulk solution.[21] Moreover, estimates of such work terms are seldom available for reactions following inner-sphere pathways.

For surface-attached (or adsorbed) reactants, a "unimolecular" rate constant k_a^E (sec^{-1}) can be determined that is related to k_{sol}^E by[19,20]

$$k_{sol}^E = K_p k_a^E = K_o k_a^E \exp(-\Delta G_p^\circ / RT) \qquad (8)$$

where K_p is the equilibrium constant (cm) for forming the precursor (surface-attached) state from the bulk reactant, and K_o is the value of K_p when $\Delta G_p^\circ = 0$. Consequently, for the one-electron reduction of an adsorbed reactant we can write from Eq. (3)

$$RT \ln k_a^E = RT \ln A_a - \Delta G_{int}^* - \alpha(\Delta G_s^\circ - \Delta G_p^\circ) - \alpha F(E - E_{sol}^f) \qquad (9)$$

where A_a ($= A_{sol}/K_o$) is a frequency factor (sec^{-1}) for activation *within the adsorbed state*, i.e. the frequency with which the elementary barrier is surmounted. Equation (9) can be simplified by noting that the formal potential in the surface-attached state E_a^f will differ from E_{sol}^f according to

$$E_a^f = E_{sol}^f + RT(\ln K_p - \ln K_s)$$

$$= E_{sol}^f + (\Delta G_s^\circ - \Delta G_p^\circ)/F \qquad (10)$$

where K_s is the equilibrium constant for forming the successor state from the bulk product. This allows Eq. (9) to be written as

$$RT \ln k_a^E = RT \ln A_a - \Delta G_{int}^* - \alpha F(E - E_a^f) \qquad (11)$$

Therefore the "real" activation enthalpy $\Delta H_{r,a}^*$ obtained from the temperature dependence of k_a measured at E_a^f at each temperature, k_a°, can be expressed simply as (cf. Eq. (4)):

$$\Delta H^*_{r,a} = -R\left[\frac{d \ln k^o_a}{d(1/T)}\right] = \Delta H^*_{int} \tag{12}$$

The preexponential factor A'_a obtained from

$$k^o_a = A'_a \exp(-\Delta H^*_{r,a}/RT) \tag{13}$$

is related to the theoretically significant quantity A_a simply by (cf. Eqs. (6) and (7))

$$A'_a = A_a \exp(\Delta S^*_{int}/R) \tag{14}$$

Therefore in contrast to the activation parameters for solution reactants, the desired intrinsic enthalpic barrier and frequency factor can be obtained from the experimental quantities for adsorbed reactants without requiring additional information on the thermodynamic stabilities of the precursor and successor states. Moreover, the intrinsic entropic barrier ΔS^*_{int} in Eq. (14) is predicted from electron-transfer theories to be small $(0 \pm 10 \ J \cdot deg^{-1} \ mol^{-1})$[16,22]; i.e., the contributions to ΔG^*_{int} arising from solvent repolarization as well as inner-shell reorganization are almost independent of temperature. Indeed, this conclusion can be deduced on purely intuitive grounds since the degree of solvent polarization around the redox center within the transition state is expected to be appropriately intermediate between that for the precursor and successor states.[16] This enables the frequency factor A_a to be determined directly using Eq. (10) from the experimental values of k^o_a and $\Delta H^*_{r,a}$. Also, since $\Delta G^*_{int} = \Delta H^*_{int} - T\Delta S^*_{int}$, in view of Eq. (12) $\Delta H^*_{r,a}$ can be approximately identified with the intrinsic barrier ΔG^*_{int}. This markedly closer relationship of the experimental activation enthalpy and preexponential factor to the desired intrinsic barrier and frequency factor for adsorbed reactants in comparison with the corresponding measured quantities for solution-phase reactants arises simply because the former experimental quantities refer

directly to the elementary electron-transfer step itself rather than to the multi-step process involved in the formation of bulk products from bulk reactants.

Values of k_a^o and $\Delta H_{r,a}^*$ are clearly inaccessible for attached redox couples for which E_a^f cannot be determined, such as those for which the product is rapidly desorbed, irreversibly decomposes, or undergoes a multiple step reaction such as coupled electron and proton transfer. However, estimates of A_a may still be extracted from "ideal" activation enthalpies $\Delta H_{i,a}^*$ obtained from an Arrhenius plot of $\ln k_a$ versus $(1/T)$ measured at a constant electrode potential using the nonisothermal cell configuration. The values of $\Delta H_{i,a}^*$ and k_a at a given electrode potential are related to A_a by (cf. Eqs. (13), (14)):

$$k_a = A_a \exp(\Delta S_{i,a}^*/R) \exp(-\Delta H_{i,a}^*/RT) \qquad (15)$$

The "ideal" activation entropy $\Delta S_{i,a}^*$ will generally differ from zero since in addition to the intrinsic entropic term ΔS_{int}^* it contains a contribution from the entropic driving force for the electron-transfer step. Thus from Eqs. (2) and (7):

$$\Delta S_{i,a}^* = \Delta S_{int}^* + \alpha_I(\Delta S_{rc}^o + \Delta S_s^o - \Delta S_p^o) \qquad (16a)$$

$$= \Delta S_{int}^* + \alpha \Delta S_{et}^o \qquad (16b)$$

Providing that the entropic work terms ΔS_s^o and ΔS_p^o are approximately equal, the value of $\Delta S_{i,a}^*$ required in Eq. (15) can therefore be estimated from experimental values of ΔS_{rc}^o measured for structurally similar redox couples.[23] The results of such an analysis for the irreversible reduction of adsorbed Cr(III) and Co(III) complexes at various metal surfaces will be presented elsewhere.[24]

The relationship between the various activation enthalpies noted here, $\Delta H_{r,sol}^*$, $\Delta H_{r,a}^*$, and $\Delta H_{i,a}^*$, are shown schematically in Fig. 1 in the form of potential-energy surfaces. The states Ox, P, A, S, and Red along the reaction coordinate refer to the bulk oxidized, precursor, activated, successor, and bulk reduced states, respectively. Curve 1 illustrates the actual potential-energy surface at a potential equal to E_a^f. The elementary step (PAS) is enthalpically "uphill" by an amount equal to $T\Delta S_{et}^\circ$ since $\Delta H_{et}^\circ = T\Delta S_{et}^\circ$ at E_a^f, so that the measured "ideal" activation enthalpy $\Delta H_{i,a}^*$ will contain a contribution from the driving force $\alpha T\Delta S_{et}^\circ$. Curve 2 shows the potential energy surface corresponding to the "real" activation enthalpy $\Delta H_{r,a}^*$ also measured at E_a^f. Note that the driving force component $T\Delta S_{et}^\circ$ is now absent. It is important to recognize that curve 1 and not curve 2 represents the actual potential energy surface at E_a^f. Curve 2 represents instead the surface corresponding to the electrode potential where $\Delta H_{et}^\circ = 0$, i.e. where the elementary step is "thermoneutral" so that $\Delta H_{r,a}^* = \Delta H_{int}^*$ (Eq. (12)). Also shown in Fig. 1 is the surface corresponding to the "real" activation enthalpy $H_{r,sol}^*$ measured for the solution reactant at E_{sol}^f (curve 3). Note that now the states Ox and Red are isoenergetic rather than P and S as in curve 2. Consequently $\Delta H_{r,sol}^*$ will differ from $\Delta H_{r,a}^*$ not only by virtue of the precursor work term ΔH_p°, but also because states P and S for curve 3 will differ in energy when $\Delta H_p^\circ \neq \Delta H_s^\circ$. These two factors are responsible for the two components, ΔH_p° and $\alpha_I(\Delta H_s^\circ - \Delta H_p^\circ)$, by which $\Delta H_{r,sol}^*$ differs from ΔH_{int}^* (Eq. (4)).

Significance of Frequency Factor for Attached Reactants

The determination of A_a is of particular interest since it provides a measure of the frequency with which electron transfer occurs once the configuration of the nuclear coordinates appropriate for electron transfer has been achieved. The usual collision frequency is clearly inappropriate for treating the reaction

of an attached molecule.[25] One suggestion has been to use instead the

characteristic frequency of the electron in the metal electrode (ca. 10^{15} sec^{-1}).[7]

Although this frequency might be useful in calculating an electron tunneling

probability or describing certain activationless reactions, it is an

incorrect choice in most cases because it ignores the much slower processes

involved in surmounting the Franck-Condon barrier.

A recent "semi-classical" treatment of electron transfer[26] provides an

enlightening description of the physical processes that influence such

frequency factors. Although concerned with homogeneous electron transfer,

the model described in ref. 26 can also be applied to electrochemical

reactions. We can express A_a as[26]

$$A_a = \kappa_{el} \Gamma_n \nu_n \tag{17}$$

where κ_{el} is an electronic transmission coefficient, Γ_n is a nuclear tunneling

factor and ν_n is a nuclear frequency factor. This last term is viewed as

the frequency with which the transition state is approached from the precursor

state. Since activation results from solvent reorganization and bond

stretching (or compression), ν_n is taken as an appropriately weighted average

of the frequencies of these two processes.[26] We can write:[26]

$$\nu_n^2 = \frac{\nu_s^2 \Delta G_s^* + \nu_i^2 \Delta G_i^*}{\Delta G_s^* + \Delta G_i^*} \tag{18}$$

where ν_s and ΔG_s^* are the frequency and activation free energy associated with

solvent reorganization, and ν_i and ΔG_i^* are the corresponding quantities associated

with bond vibration. Taking $\nu_s \approx 10^{11}$ sec^{-1} in water[26] and $\nu_i \approx 10^{13}$ sec^{-1} as

a typical bond stretching frequency yields $\nu_n \approx 10^{12}$ to 10^{13} sec^{-1},

if, as usual, bond reorganization is a significant contributor ($\geqslant$1%) to the

overal^1 reorganization energy. This result is numerically similar to the conventional frequency factor kT/h at ambient temperatures.

The nuclear tunneling factor Γ_n in Eq. (17) accounts for the contribution to the reaction rate arising from electron transfer involving vibrational states that lie below the free energy intersection region. It is close to unity for small values of ΔG_i^*. Although $\Gamma_n > 1$, it generally increases with decreasing temperature,[26] thereby decreasing the measured values of ΔH^* and hence yielding smaller apparent values of A_a. However, the effect is calculated to be negligible at ambient temperatures for reactions where $\Delta G_i^* \lesssim 40$ kJ mol^{-1}.[26]

The only other contributor to A_a is the electron tunnelling term κ_{el}, which is unity for an adiabatic reaction. Therefore any discrepancies between experimental values of A_a and the corresponding calculated values of ν_n may normally be attributed to a small value of κ_{el}. Thus contrary to some recent statements,[7,8] the observation that $A_a \ll 10^{13}$ sec^{-1} or, equivalently, of large negative activation entropies obtained from $\Delta H_{r,a}^*$ by assuming that $A_a \sim 10^{13}$ sec^{-1} [Eqs. (13), (14)] can be taken as evidence that $\kappa_{el} \ll 1$.

Objections that the Marcus and other electron-transfer models based on "absolute reaction rate" theory do not apply to surface-attached reactants[7] are incorrect; no extra assumptions are made in applying contemporary theories to these reactions besides the choice of an appropriate statistical formalism for the frequency factor. In fact, redox processes involving surface-attached reactants are in some respects better model reactions for testing electron-transfer theories than are outer-sphere electrochemical reactions. Since the surface-attached reactant and product can be identified with the precursor and successor states, both the thermodynamics and kinetics of the elementary electron-transfer step are susceptible to direct experimental determination. As noted above, this is strictly not the case for outer-sphere reactions, so that the intrinsic barrier ΔH_{int}^* and frequency factor A_{sol}

can only be obtained from the experimental kinetics parameters by estimating

the enthalpic and entropic work terms [Eqs. (4)-(7)].

In addition, for outer-sphere reactions there is a substantial uncertainty

regarding the theoretical formulation of A_{sol} and its relation to the frequency

factor for the elementary step. The conventional collisional model predicts a

typical value of A_{sol} of $\sim 5 \times 10^3$ cm sec^{-1}.[16] The alternative "pre-equilibrium"

model [Eq. (7)][10,20,27] describes the frequency factor as a product of an

equilibrium constant K_p for the formation of a precursor state from the bulk

reactant, and a frequency ν_n for solvent reorganization and bond vibrations as

in Eq. (18). Significantly larger values of A_{sol}, around 5×10^5 cm sec^{-1},

can be derived using this model.[11,20] However, there is a significant

uncertainty in K_p and hence A_{sol}, arising from the lack of information on the

effective thickness of the precursor state "reaction zone" within which the

reactant is required to reside so that electron tunneling can occur

with sufficient probability to contribute to the reaction rate.[11,20] These

uncertainties regarding the theoretically expected values of A_{sol} lead to

difficulties in separating out the various other contributions to the experimental

frequency factors. Such difficulties are absent for reactions of surface-

attached molecules.

It is interesting to note that the advantages that are expected in the

study of attached molecule reactions as compared to solution electrochemical

reactions have close parallels in studies of homogeneous electron transfer.

Thus, rate data and activation parameters for intramolecular electron-

transfer reactions in bridged binuclear complexes are more easily interpreted

than are the corresponding results for the usual second order outer-sphere

reactions.[28] The problems associated with the choice of an appropriate

theoretical formalism for the frequency factor, and the uncertainties in the

work term corrections[29] are absent for intramolecular reactions. The treatment

of electron transfer between an attached reactant and an electrode surface

contains closely analogous advantages and can usefully be perceived as a heterogeneous "intramolecular" reaction.[10,11]

Studies of electron-transfer kinetics between surface-bound molecules and electrodes as a function of temperature are as yet uncommon.[5,7,8,24] Brown and Anson have determined that $A'_a = 10^6$ sec^{-1} for the reduction of 9,10-phenanthrenequinone at graphite.[5] However, this reaction involves a proton-transfer step preceding electron transfer which precludes extraction of the true frequency factor A_a in the absence of thermodynamic data for the former equilibrium. Sharp and coworkers have obtained some interesting results for the ferrocene/ferricinium couple bound to a platinum electrode.[7,8] Values of $k°_a$ for this couple were reported as a function of temperature in acetonitrile and sulpholane. The frequency factor A'_a was reported to be 3×10^8 sec^{-1} in acetonitrile[7] and 2×10^8 sec^{-1} in sulpholane.[8] Assuming that the inner-shell reorganization ΔG^*_i comprises about 5% of the total reorganization energy,[7] and ν_{in} and ν_{out} are $\sim 10^{13}$ sec^{-1} and $\sim 2 \times 10^{11}$ sec^{-1}, respectively, ν_n is estimated to be about 2×10^{12} sec^{-1}. From the usual dielectric continuum expression neglecting the influence of the reactant-electrode image interactions[16] and using literature values of the optical and static dielectric constants and their temperature derivatives[30-32] ΔS^*_{int} is calculated to be -12 J deg^{-1} mol^{-1} in acetonitrile and -7 J deg^{-1} mol^{-1} in sulpholane. From these values of A_a and ν_n using Eqs. (14) and (17), estimates of κ_{el} of about 6×10^{-4} in acetonitrile and 2×10^{-4} in sulpholane are obtained, indicating that the electron-transfer reaction is moderately nonadiabatic under these conditions.

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<u>Figure Caption</u>

Schematic potential-energy surfaces for a single-step electrode reaction, illustrating the distinction between "real" and "ideal" activation enthalpies for attached reactants (see text for details).

FIGURE 1

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$\Delta H^{*}_{r,sol}$

$\Delta H^{*}_{r,a}$

$\Delta H^{*}_{i,a}$

A

$T\Delta S^{\circ}_{et}$

2

3

1

Ox   P   S   Red

Nuclear Reaction Coordinate

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